Density Functional Study of the Ground and Excited State Potential Energy Surfaces of a Light-Driven Rotary Molecular Motor (3R,3 ' R)-(P,P)-trans-1,1 ',2,2 ',3,3 ',4,4 '-Octahydro-3,3 '-dimethyl-4,4 '-biphenanthrylidene

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A density functional study of the ground and excited state potential energy surfaces of a light-driven rotary molecular motor (3R,3'R)-(P,P)-trans-1,1',2,2',3,3',4,4'-octahydro-3,3'-dimethyl-4,4'-biphenanthrylidene.

Supporting information.

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Table 1: The geometry parameters of the (3R,3'R)-(P,P)-trans-1,1',2,2',3,3',4,4'-octahydro-3,3'-dimethyl-4,4'-biphenanthrylidene molecular motor (see scheme 1 for the labels) in the four conformations: (P,P)-*trans*-**1**, (M,M)-*cis*-**2**, (P,P)-*cis*-**2**, (M,M)-*trans*-**1** (denoted in the table as PPT, MMC, PPC, MMT, correspondingly), optimized with B3LYP using two different basis sets and the relative B3LYP ground state energies with respect to PP-trans conformation in eV. The experimental values [1] are shown in brackets

	6-31G*/STO-3G				6-31G*			
	PPT	MMC	PPC	MMT	PPT	MMC	PPC	MMT
α	186.6	-17.8	2.2 (-3.2)	160.1	188.6	-17.6	0.9 (-3.2)	161.1
α'	-165.6	-21.2	5.4 (5.9)	151.7	-164.0	-22.7	7.2 (5.9)	150.8
β	67.1	-46.1	54.1 (54.4)	-44.0	68.6	-48.2	56.1 (54.4)	-45.1
γ	-121.8	-41.8	-94.3 (-97.0)	-44.8	-118.9	-40.3	-95.1 (-97.0)	-44.1
γ'	-121.8	-41.8	-94.3 (-96.0)	-44.8	-118.9	-40.3	-95.1 (-96.0)	-44.1
ζ	190.5	178.3	181.6	175.8	192.3	177.4	183.1	174.8
φ	124.3	120.7	124.4	122.1	123.7	120.9	124.9	122.1
1	1.356	1.377	1.362 (1.347)	1.378	1.357	1.377	1.361 (1.347)	1.378
2	1.495	1.500	1.494	1.495	1.494	1.498	1.493	1.492
3	1.399	1.402	1.400	1.406	1.393	1.396	1.394	1.399
4	1.523	1.520	1.523	1.520	1.509	1.506	1.509	1.506
5	1.569	1.558	1.562	1.558	1.544	1.535	1.538	1.535
6	1.580	1.562	1.569	1.556	1.570	1.551	1.558	1.545
7	1.532	1.559	1.541	1.563	1.532	1.557	1.540	1.559
ΔE	0.00	0.56	-0.01	0.45	0.00	0.62	0.03	0.43

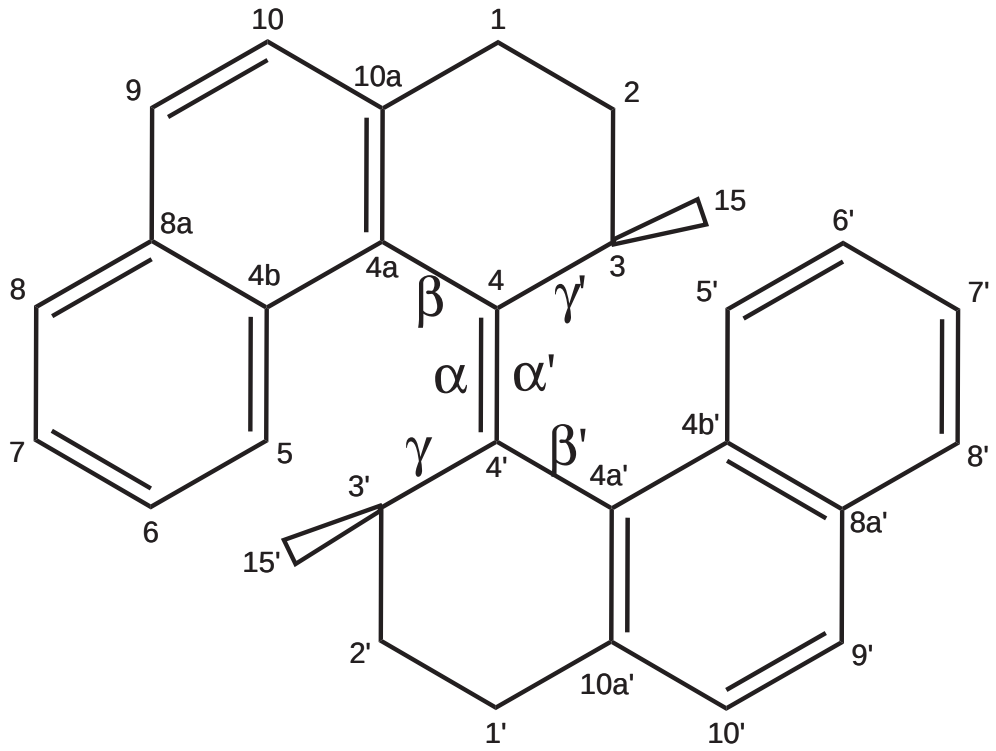
Table 2: The vertical excitation energies in the (P,P)-*trans*-**1** and (P,P)-*cis*-**2** conformations. The geometries optimized with two different basis sets[a] were used. The excitation energies were calculated with the use of TD-BH&HLYP and SA-REBH&HLYP and three different basis sets[b]. Deviations from the experimental data are shown. All energies are in eV.

	SA-REKS				TDDFT			
	A		B		A		B	
(P,P)-*trans*-**1**								
	S_1-S_0	Error	S_1-S_0	Error	S_1-S_0	Error	S_1-S_0	Error
1	4.87	0.81	4.88	0.82	4.79	0.73	4.80	0.74
2	4.47	0.41	4.50	0.44	4.27	0.21	4.30	0.24
3	4.41	0.35	4.44	0.38	4.19	0.14	4.23	0.17
Exp.[c]	4.06		4.06		4.06		4.06	
(P,P)-*cis*-**2**								
	S_1-S_0	Error	S_1-S_0	Error	S_1-S_0	Error	S_1-S_0	Error
1	4.65	0.44	4.65	0.44	4.63	0.42	4.63	0.42
2	4.23	0.02	4.29	0.08	4.17	-0.04	4.20	-0.01
3	4.18	-0.03	4.24	0.03	4.10	-0.11	4.14	-0.07
Exp.[c]	4.21		4.21		4.21		4.21	

[a] A: REB3LYP/hybrid 6-31G*/STO-3G optimized structures; B: REB3LYP/6-31G* optimized structures.

[b] 1: hybrid 6-31G*/STO-3G; 2: 6-31G*; 3: 6-311G**

[c] Cited from Ref. [1].



α=(4a, 4, 4',4a'); α'=(3, 4, 4',3')
β=(4', 4, 4a,4b); β'=(4, 4', 4a',4b')
γ=(4, 4', 3',15'); γ'=(4', 4, 3,15)
ζ=(3, 4, 4',4a); φ=(3, 4, 4')
1=44'; 2=44a; 3=4a10a;
4=10a1; 5=12; 6=23; 7=34

Scheme 1:

References

[1] Harada, N. ; Koumura, N.; Feringa, B. L. *J. Am. Chem. Soc.* **1997**, *119*, 7256.